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## **Ambient air measurements related to traffic : evolution of VOCs over three years**

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### **Abstract**

*Influence of traffic emission on air quality in European cities has widely been studied. Nevertheless, measurement campaigns are usually limited. We present here a set of VOC measurements which has been collected during 5 to 6 campaigns each year over three years. Ambient air is sampled outside vehicles, inside the traffic. Evolution of the concentrations both in urban and rural air over the 3 years are discussed, compound by compound, and compared to data from literature. Influence of traffic on concentrations is obvious. The major finding is that the concentrations of pollutants related to traffic have been decreasing between 2003 and 2005, specially in urban atmospheres, and in a lesser way, in rural areas.*

**Keys-words :** air quality, traffic, VOCs, greater Paris area.

### **Résumé**

**Mesures d'air ambiant en conditions de trafic : évolution des COV sur 3 ans.**

*L'influence des émissions liées au trafic automobile sur la qualité de l'air a largement été étudiée. Cependant, les campagnes de mesures sont généralement limitées, dans la durée et le nombre de composés étudiés. Nous présentons ici les résultats d'un ensemble de campagnes réalisées sur une durée de 3 ans, sur plusieurs composés organiques volatils. Le prélèvement est réalisé à l'extérieur de véhicules en roulage, dans la Région Parisienne, en milieux urbain et semi-rural. L'évolution des concentrations au cours du temps est discutée, et les teneurs sont comparées aux données de la littérature. Le fait marquant est la diminution très importante entre 2003 et 2005 des teneurs pour une majorité des polluants, surtout en milieu urbain, et dans une moindre mesure en milieu rural. La diminution de la teneur en benzène des essences, ainsi que l'amélioration des moteurs et le développement des pots catalytiques, explique largement cette tendance.*

**Mots-clés :** qualité de l'air, trafic, COV, Région Parisienne.

### **Introduction**

Influence of traffic emission on air quality in European cities has widely been studied. Nevertheless, measurement campaigns are usually limited, in the number of pollutants or in the time scale. We present here a set of atmospheric measurements of volatile organic compounds which has been collected outside a car, driving in the traffic, during 5 to 6 campaigns each year between 2003 and 2005. All the parameters: compounds, sampling and analytical techniques, locations, remained the same over the three years, allowing us to study the evolution of concentrations. This evolution is discussed for urban and rural air, and values are compared to data from literature.

### **1 - Experimental**

Outside air inlet is fixed on the front trunk of the car, near the car air inlet. A Teflon tubing goes to the inside of the car, where different apparatus are connected. Sampling is done while the vehicle is moving, on public roads, with two different routes : one is typically urban, most of the journey takes place on the Parisian Peripherique (motorway around Paris, limited speed 80 km/h), the other one is semi-rural, in the south-west of greater Paris area (2 lanes roads, limited speed 90 km/h except in the villages : 50 km/h). The same air flow is split to the different sampling systems. The overall sampling time is around three hours.

The major VOC are : benzene and toluene, MTBE, 1,3-butadiene, formaldehyde, phenol, naphtalene. Other compounds of the same families (BTEX, aldehydes and PAH) are analysed in the same time, but will not be discussed here.

Aromatic hydrocarbons and MTBE are sampled by pumping the air through Carbotrap 300™ glass tubes, loaded with Carbotrap/ Carbosieve S III adsorbents. The sampled volume is 3,6 litres. Tubes are extracted by thermal desorption on a Perkin Elmer Turbomatrix, and analysed by GC/FID.

1,3-butadiene is sampled in evacuated Silcocan™ canisters of 6 litres. Extraction and analysis are performed within the following week. 2 litres of air from the canisters are trapped on Carbotrap/Carbosieve Perkin Elmer tubes. Tubes are thermally desorbed and analysed by GC/FID.

Formaldehyde is sampled by pumping on SEP-PAK™ : DNPH-silica gel cartridges. Sample volume is 36 litres. Extraction is done by solvent desorption. Analysis is done by HPLC with UV detection).

Phenol is sampled on 2-zones solid adsorbents of ORBO type; two tubes are placed in series. Sampling volume is 100 litres. Desorption of each individual zone is done by NaOH 0,1 N. Analysis is performed with HPLC with fluorescence detection at 274/298 nm.

Polycyclic aromatic compounds (PAH) are sampled on quartz membranes + XAD-2 resin. Sampling volume is 275 litres. Extraction of supports taken together is done by ultrasonic bath, then extract. is concentrated. Analysis is done by HPLC/UV fluorescence with specific PAH wavelengths. On these samples, we only detect the 6 lighter PAH : naphtalene to fluoranthene.

## **2 – Results and discussion**

We present here the results of 16 measurement campaigns, distributed over the period March 2003 – November 2005. “ZERO” concentrations are lower than quantification limits.

### **Benzene**

Figure 1 gives the benzene concentrations for urban and rural journeys.

The first observation is that benzene concentrations tend to decrease since March 03. This fact has been reported by several authors (Simon et al, Stemmler et al), as well as by the French air quality network for the greater Paris area “AIRPARIF”. This decrease is due to the reduction of benzene in gasoline, and, like for the other VOC's, to the generalisation of exhaust catalysts on cars, since 1993 for gasoline-fuelled cars, and 1997 for diesel-powered cars. Only the last campaign - November 2005 – shows a slightly higher value than the previous ones. There has been a pollution episode at this time : AIRPARIF measurements on the edge of the Peripherique at Porte d'Auteuil, on the day of the campaign, show values which are consistent with those we measured in the traffic.

Second fact is that all urban concentrations except one, taken inside the traffic, exceed the future European Limit Value to be attained in 2010, of 5 µg/m<sup>3</sup> (EC Directive 2000/69/EC). This limit value is an annual mean. Fortunately, benzene concentrations are lower at night, and also lower in areas with less cars, like quiet streets and residential areas, so the mean daily exposure, for a citizen, generally fulfils this limit value.

On the contrary, nearly all our benzene measurements in the rural area comply with the French Air

Quality Guideline of  $2 \mu\text{g}/\text{m}^3$  (Décret n° 98-360 du 6 mai 1998, JORF 13 mai 1998). The decrease in concentration with time is not so obvious as for urban air, because values are lower. In fact, rural benzene concentrations were sometimes lower than our quantification limit.

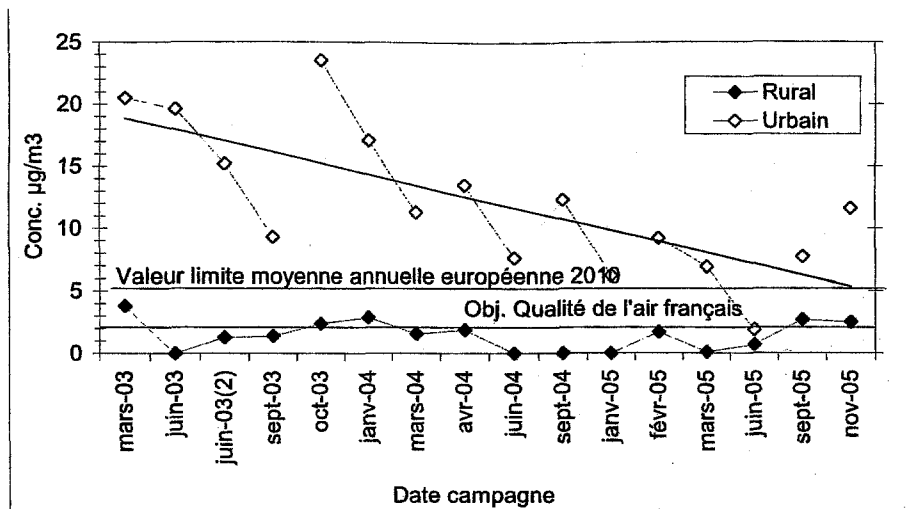


Figure 1 : concentrations en benzène relevées sur les 16 campagnes (urbain + rural)

*Figure 1 : benzene concentrations for the 16 campaigns (urban + rural)*

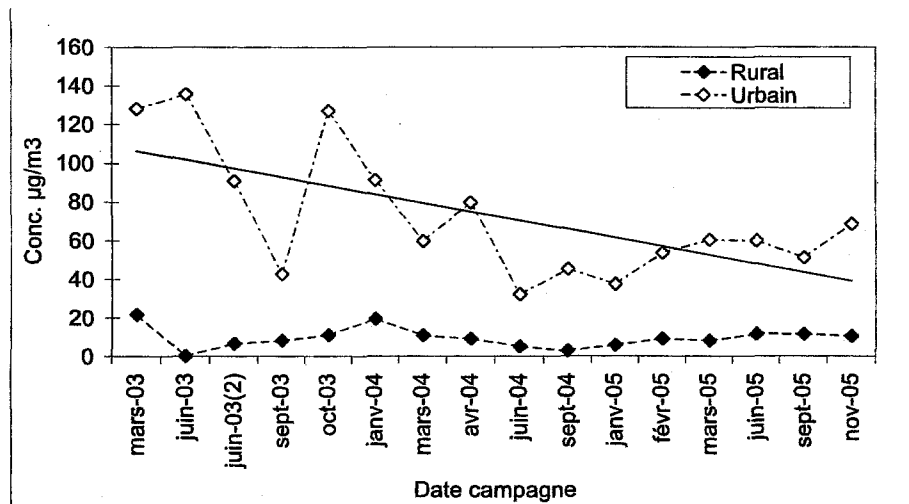


Figure 2 : concentrations en toluène relevées sur les 16 campagnes (urbain + rural)

*Figure 2 : toluene concentrations for the 16 campaigns (urban + rural)*

## Toluene

Figure 2 gives the toluene concentrations for urban and rural journeys.

Toluene concentrations are quite high in urban air : they vary between 32 and more than  $120 \mu\text{g}/\text{m}^3$ . Such values have been reported for the same type of sampling in Birmingham (Leung & Harrison). Rural concentrations are generally in between  $5$  and  $15 \mu\text{g}/\text{m}^3$ , which is slightly higher than other European values (Keymeulen et al, Schneider et al) but the sampling here is done in the “rural” part of the greater Paris area, therefore a small influence of the city is possible.

As for benzene, we see a overall tendency to decrease with the time since March 03. The stable values over the last year need to be confirmed. They could probably be due to the opposite effect offleet renewal with cars emitting less pollutants, and the increase of traffic, and traffic jams, in Paris and closer suburbs.

## Toluene/benzene ratios

Table 1 gives the toluene/benzene ratio for urban air samples. Generally, for urban air sampled in

cities, with a BTX pollution coming mainly from the traffic, the toluene/benzene ratio is in-between 2 and 3. It is lower when the air mass is aged : in a Greek city, at 50 meters above the traffic, this ratio is in-between 0.7 and 0.97 (Pilidis and al). Here, sampling is done closer to the source : the car exhaust, and there is no time for the pollutants to react with the radicals presents in the air. Therefore, toluene concentrations are higher than in an older air mass.

Dates	mars-03	juin-03	juin-03 (2)	sept-03	oct-03	janv-04	mars-04	avr-04	juin-04
Toluène/Benzène	6,3	6,9	6,0	4,6	5,4	5,3	5,3	5,9	4,2

Dates	sept-04	janv-05	févr-05	mars-05	juin-05	sept-05	nov-05	Moyenne	$\sigma$
Toluène/ Benzène	3,7	6,0	5,8	8,7	--	6,6	5,9	5,8	1,2

Tableau 1 : rapports des concentrations toluène/benzène pour les 16 campagnes (roulages urbain)

Table 1 : toluene/benzene ratio for the 16 campaigns (urban routes only)

Composé	Date	mars-03	juin-03	jun-03 (2)	sept-03	oct-03	janv-04	mars-04	avr-04	juin-04	sept-04	janv-05	févr-05	mars-05	juin-05	sept-05	nov-05
MTBE	Rural	ND	0	1	1,9	2,2	3	0	4,2	2,9	1,5	3,9	5,6	3,5	0,7	1,8	1,4
	Urbain	ND	30	16	ND	21	12	7,7	31	7,9	16	13	32	18	4,7	16	18
1,3-butadiène	Rural	0,1	0,3	0	0	0,6	0,6	0,2	0	0	0,2	0	0	ND	0,2	0,1	0,7
	Urbain	1,4	0,8	0,2	0,4	3,3	2,2	1,2	0,1	0,9	0,1	0	0,3	ND	1,5	0,4	3,0

Tableau 2 : concentrations ( $\mu\text{g}/\text{m}^3$ ) en MTBE et 1,3-butadiène, pour les 16 campagnes

Table 2 : concentrations ( $\mu\text{g}/\text{m}^3$ ) for MTBE and 1,3-butadiène, on the 16 campaigns

### Other pollutants

Table 2 gives the concentrations in MTBE and 1,3-butadiene.

For MTBE, urban concentrations vary widely from one campaign to another : from 5 to  $32 \mu\text{g}/\text{m}^3$ . Rural values are more constant, and, like benzene and toluene, much lower than in urban area: they vary from zero (concentration under quantification limit) to  $6 \mu\text{g}/\text{m}^3$ . There is no obvious season effect on the higher urban concentrations. This compound, which is an additive in gasoline, is not very often measured in Europe. Mean weekly values reported for Helsinki (Hellen et al) are lower than  $2 \mu\text{g}/\text{m}^3$ .

For 1,3-butadiene, concentrations are low, even for urban air. Values are lower than  $2 \mu\text{g}/\text{m}^3$ , except for two cases in October 03 and November 05 : for the latter, it is the same behaviour as benzene, toluene and MTBE. These values, though being measured inside the traffic, fall within the English Air Quality Objective of  $2,25 \mu\text{g}/\text{m}^3$  as an annual mean (UK National Air Quality Strategy). Rural concentrations are all lower than  $1 \mu\text{g}/\text{m}^3$ . There is no obvious season effect, though butadiene concentrations should be lower in summer due to the reaction of this compound with ozone (Liu et al). There is no obvious decrease effect either, except between October 03 and February 05, but we have encountered higher values since then.

Figure 3 gives the concentration for formaldehyde. Except in January and November 05, for which urban concentrations are relatively high, urban and rural concentrations show the same tendency, and rural concentrations are 2 to 3 times lower than urban concentrations. Values are generally higher than the mean value measured in Paris in 2003, probably at background sites :  $4,3 \mu\text{g}/\text{m}^3$  (LCPP). This means that the source is anthropogenic and urban. Concentrations are lower in summer because of reactions with ozone, in air and during sampling, which causes an underestimation in formaldehyde.

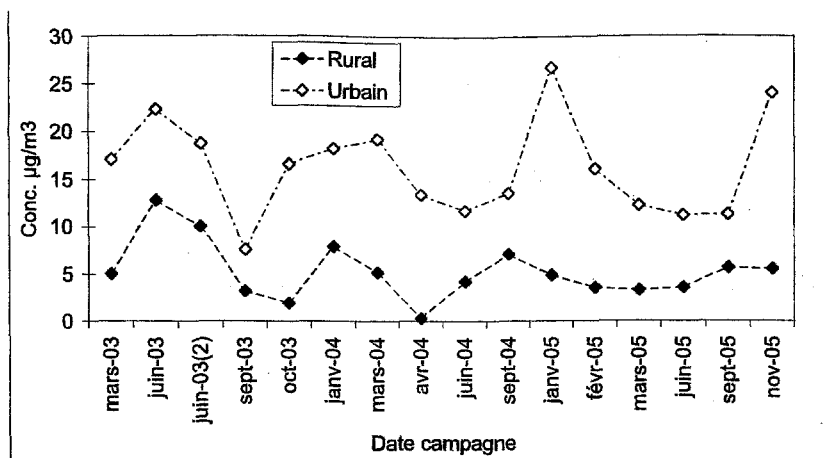


Figure 3 : concentrations en formaldéhyde relevées sur les 16 campagnes (urbain + rural)

Figure 3 : formaldehyde concentrations for the 16 campaigns (urban + rural)

Figure 4 gives the concentrations for phenol. This pollutant is not often measured in ambient air and concentrations are generally low. Here, we report concentrations between 0 (below quantification limits) and 2  $\mu\text{g}/\text{m}^3$ . Once again, urban values are higher than rural concentrations, and they both tend to decrease with time, especially for urban values. There are little data available on phenol in ambient air. Inchem monograph cites values in Paris (1978 to 1985) from 0,7 to 8  $\mu\text{g}/\text{m}^3$ . Our measurements, though taken inside the traffic, do not show so high values.

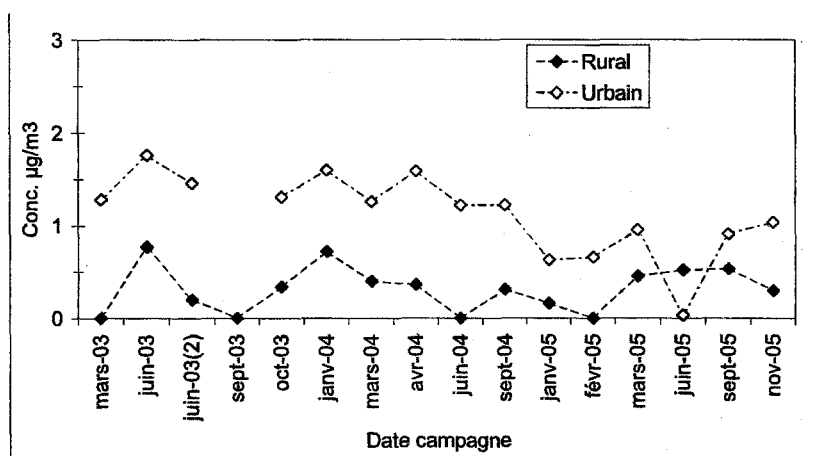


Figure 4 : concentrations en phénol relevées sur les 16 campagnes (urbain + rural)

Figure 4 : phenol concentrations for the 16 campaigns (urban + rural)

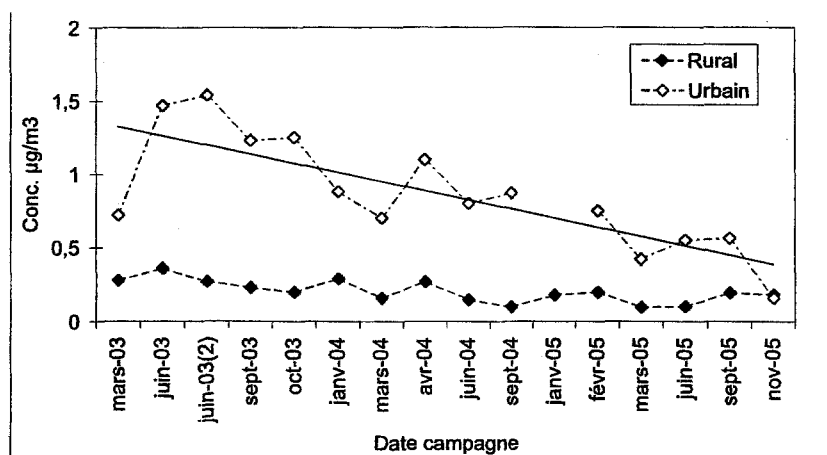


Figure 5 : concentrations en naphtalène relevées sur les 16 campagnes (urbain + rural)

Figure 5 : naphthalene concentrations for the 16 campaigns (urban + rural)

Figure 5 gives the concentrations for naphthalene. It is the lighter of the PAH, therefore the one which will have the closest behaviour to the VOCs. As for the aromatic compounds, we see clearly a decrease since March 2003, but this decrease has been going on continuously over the last year. There is an increasing number of diesel engine cars in France : more than half the new cars sold nowadays, and all the light and heavy duty vehicles, are diesel powered. The particulate matter and the PAH in the air should therefore be increasing. The observed decreasing tendency can be explained by the benefit of fleet renewal with new technologies (Filter trap, ...) able to decrease the PM and gas emissions.

## Conclusion

For all the pollutants that we presented here, influence of traffic as one of the major sources is obvious : rural concentrations are far lower than urban values. Though our measurements are taken right in the traffic, concentrations for several compounds are rather low compared to some of the published data. It is directly connected to an improvement in air quality in a large city like Paris.

The major finding is that the concentrations of most pollutants have been decreasing dramatically between 2002 and 2004, despite an increase in traffic, specially in urban atmospheres, and to a lesser extend, in rural areas as well. There are several causes : reduction of benzene in gasoline, improvement of engines, limitation of emissions thanks to catalysts, and renewal of the car fleet. Only formaldehyde, MTBE and 1,3-butadiene do not show this decrease, probably due to an initial low emission rate of traffic.

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